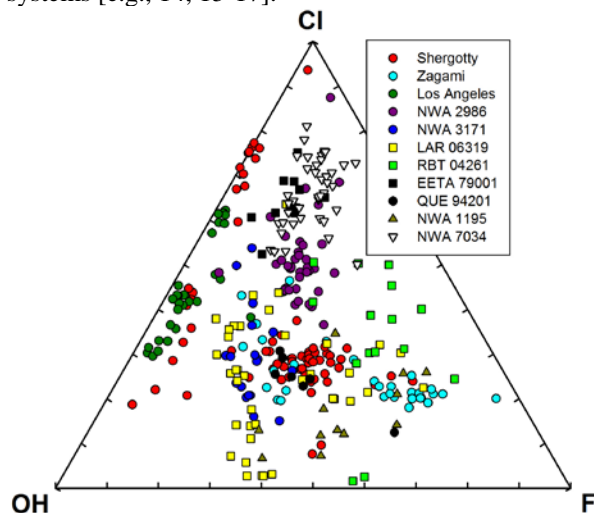


# HYDROGEN ISOTOPIC COMPOSITION OF APATITE IN NORTHWEST AFRICA 7034: A RECORD OF THE “INTERMEDIATE” H-ISOTOPIC RESERVOIR IN THE MARTIAN CRUST? F. M. McCubbin<sup>1</sup>, J. J. Barnes<sup>2</sup>, A. R. Santos<sup>3</sup>, J. W. Boyce<sup>4</sup>, M. Anand<sup>2,5</sup>, I. A. Franchi<sup>2</sup>, and C. B. Agee<sup>3</sup>. <sup>1</sup>NASA Johnson Space Center, mailcode XI2, 2101 NASA Parkway, Houston, TX 77058. <sup>2</sup>Planetary and Space Sciences, The Open University, Milton Keynes, MK7 6AA, UK. <sup>3</sup>Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131. <sup>4</sup>Department of Earth, Planetary, and Space Sciences, University of California, Los Angeles, California 90095. <sup>5</sup>Department of Earth Sciences, The Natural History Museum, London, SW7 5BD, UK. ([francis.m.mccubbin@nasa.gov](mailto:francis.m.mccubbin@nasa.gov))

**Introduction:** Northwest Africa (NWA) 7034 and its pairings comprise a regolith breccia with a basaltic bulk composition [1] that yields a better match than any other martian meteorite to visible-infrared reflectance spectra of the martian surface measured from orbit [2]. The composition of the fine-grained matrix within NWA 7034 bears a striking resemblance to the major element composition estimated for the martian crust, with several exceptions. The NWA 7034 matrix is depleted in Fe, Ti, and Cr and enriched in Al, Na, and P [3]. The differences in Al and Fe are the most substantial, but the Fe content of NWA 7034 matrix falls within the range reported for the southern highlands crust [6]. It was previously suggested by [4] that NWA 7034 was sourced from the southern highlands based on the ancient 4.4 Ga ages recorded in NWA 7034/7533 zircons [4, 5]. In addition, the NWA 7034 matrix material is enriched in incompatible trace elements by a factor of 1.2-1.5 [7] relative to estimates of the bulk martian crust. The La/Yb ratio of the bulk martian crust is estimated to be ~3 [7], and the La/Yb of the NWA 7034 matrix materials ranges from approximately 3.9 to 4.4 [3, 8], indicating a higher degree of LREE enrichment in the NWA 7034 matrix materials. This elevated La/Yb ratio and enrichment in incompatible lithophile trace elements is consistent with NWA 7034 representing a more geochemically enriched crustal terrain than is represented by the bulk martian crust, which would be expected if NWA 7034 represents the bulk crust from the southern highlands.

Given the similarities between NWA 7034 and the martian crust, NWA 7034 may represent an important sample for constraining the composition of the martian crust, particularly the ancient highlands. In the present study, we seek to constrain the H isotopic composition of the martian crust using Cl-rich apatite in NWA 7034. Usui et al., [9] recently proposed that a H isotopic reservoir exists within the martian crust that has a H-isotopic composition that is intermediate ( $\delta D$  of 1000-2000‰) between an isotopically light mantle ( $\delta D < 275‰$  [10]) and an isotopically heavy atmosphere ( $\delta D$  of 2500-6100‰ [11, 12]). Apatites in NWA 7034 occur in a number of lithologic domains, however apatites across all lithologic domains have

been affected by a Pb-loss event at about 1.5 Ga before present [5], so they are unlikely to have retained a primary composition and are more likely to have equilibrated with fluids within the martian crust that may or may not have exchanged with the martian atmosphere. Equilibration of apatite with crustal fluids is further supported by the chlorine-rich compositions exhibited by apatites in NWA 7034 in comparison to apatites from other martian meteorites (Figure 1; [13]). Cl is more hydrophilic than F, which promotes formation of Cl-rich apatite compositions in fluid-rich systems [e.g., 14, 15-17].



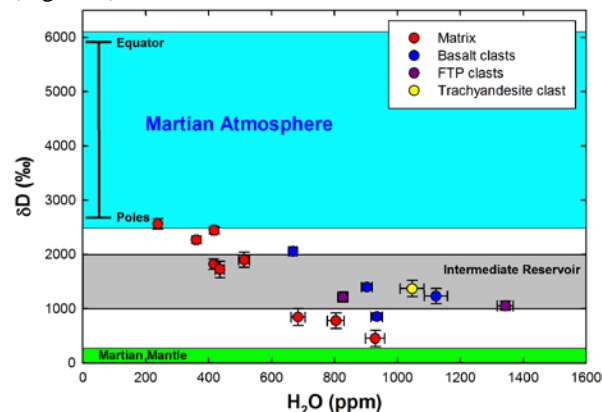
**Figure 1.** Ternary plot of apatite X-site occupancy (mol%) from all martian meteorites reported by [13]. OH was not directly measured, but it was calculated assuming  $1 - F - Cl = OH$ .

If the apatites in NWA 7034 have equilibrated with a reservoir that has undergone exchange with the atmosphere, which was postulated to be the case for the martian regolith [9], then the apatites will reflect the  $\delta D$  value of the martian atmosphere at the time that the atmosphere and regolith were equilibrated. If the apatites have equilibrated with crustal fluids, their  $\delta D$  values should reflect the composition of the martian crust, which is defined by the model of Usui et al., [9] to be in the range of 1000-2000‰. Alternatively, there could be incomplete exchange between the mantle,

crust, and atmosphere, which could result in any combination of  $\delta D$  values from  $<275\text{‰}$  to  $6100\text{‰}$ .

**Methods:** Electron probe microanalysis and back scattered electron imaging were conducted in the same manner as Santos et al., [18] and McCubbin et al., [13]. The H isotopic composition and  $H_2O$  abundance of apatite from two thin sections of NWA 7034 were measured using the Cameca NanoSIMS 50L ion probe at The Open University, following protocols described in [19]. Typically  $5 \times 5 \mu m$  areas of apatite were analyzed using a probe current of  $\sim 300$  pA. Apatite standards described in McCubbin et al., [20] were used for calibration purposes and nominally anhydrous San Carlos olivine was used to monitor background H. Real time isotope imaging was utilized to monitor for and navigate away from cracks.

**Results:** Apatites in NWA 7034 were measured in a number of lithologic contexts in NWA 7034, including basaltic clasts, Fe-Ti-P-rich (FTP) clasts, and large crystal clasts within the bulk matrix domain [18, 21]. All apatites were Cl-rich and ranged in  $H_2O$  abundances from 238-1343 ppm. In addition, the  $\delta D$  values of the apatites ranged from  $453\text{‰}$  to  $2564\text{‰}$  (Figure 2).



**Figure 2.** Plot of  $\delta D$  value vs  $H_2O$  abundance of apatites from NWA 7034. Error bars represent  $2\sigma$  uncertainties. Reservoir values for the martian atmosphere, mantle, and the intermediate reservoir are adopted from [9-12]. Clast types are described in detail by Santos et al., [18].

**Discussion:** The apatites in NWA 7034, which likely attained their final volatile inventories during a Pb-loss event at 1.5 Ga [5], have  $\delta D$  values  $<3000\text{‰}$ . This observation indicates that at least portions of the martian regolith have not exchanged completely with the martian atmosphere, which has likely had a highly fractionated  $\delta D$  value ( $>3000\text{‰}$ ) for at least 4 Ga [22]. Interestingly, all of the H-isotopic compositions of apatite in NWA 7034 fall within  $\sim 500\text{‰}$  of the range of values reported for the intermediate reservoir predicted for the martian crust by Usui et al., [9] (Figure 2). This may indicate that the H isotopic

compositions of apatite in NWA 7034 are representative of the H isotopic composition of the martian crust. A similar conclusion was recently drawn for the Cl isotopic composition of apatite in NWA 7034. Williams et al., [23] recently analyzed the  $\delta^{37}Cl$  isotopic compositions of apatite in NWA 7034 as well as the NWA 7034 bulk rock and many other martian meteorites. They report that the martian crust has a  $\delta^{37}Cl$  value of approximately  $+1\text{‰}$ , which is defined by NWA 7034, although they did find an anomalously high value of  $+8\text{‰}$  in one apatite grain. They showed that crustal contamination could be traced to a high level of accuracy using Cl isotopes and that Cl isotopes could be tracked in parallel to  $\Delta^{33}S$  anomalies [24]. Although the H and Cl isotopic compositions of apatite in NWA 7034 may be representative of the H and Cl isotopic composition of the martian crust, H isotopes do not correlate with Cl or S isotopes when the full suite of martian meteorites are considered [23-24].

Importantly, we cannot rule out incomplete exchange of H between the martian mantle and atmosphere to explain the H isotopic compositions of apatites in NWA 7034. Coordinated analyses of trace elements, Cl isotopes, and H isotopes will likely be needed to further assess whether or not the H isotopic composition of apatite in NWA 7034 represents the intermediate H isotopic crustal reservoir predicted by Usui et al., [9].

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**References:** [1] Agee C. B. et al. (2013) *Science*, 339, 780-785. [2] Cannon K. M. et al. (2015) *Icarus*, 252, 150-153. [3] McCubbin F. M. et al. (2015) *LPSC 46*, abstract #1723 [4] Humayun M. et al. (2013) *Nature*, 503, 513-516. [5] McCubbin F. M. et al. (In Review) *Geophys. Res. Lett.* [6] Boynton W. V. et al. (2007) *JGR-Planets*, 112, E12. [7] Taylor G. J. and McLennan S. M. (2008) *Planetary Crusts*, 378pp. [8] Nyquist L. et al. (2016) *MAPS*, in press. [9] Usui et al., (2015) *EPSL*, 410, 140-151 [10] Usui T. et al. (2012) *EPSL*, 357-358, 119-129. [11] Novak R. E. et al. (2011) *P&SS*, 59, 163-168. [12] Webster C. R. et al. (2013) *Science*, 341, 260-263. [13] McCubbin F. M. et al. (2016) *MAPS*, in revision. [14] Hovis G. L. and Harlov D. (2010) *Am. Min.*, 95, 946-952. [15] Meurer W. P. and Boudreau A. E. (1996) *CMP*, 125, 225-236. [16] McCubbin F. M. et al. (2013) *MAPS*, 48, 819-853. [17] McCubbin F. M. and Nekvasil H. (2008) *Am. Min.*, 93, 676-684. [18] Santos A. R. et al. (2015) *GCA*, 157, 56-85. [19] Barnes J. J. et al. (2014) *EPSL*, 390, 244-252. [20] McCubbin F. M. et al. (2012) *Geology*, 40, 683-686. [21] Muttik N. et al. (2014) *Geophys. Res. Lett.*, 41, 8235-8244. [22] Greenwood J. P. et al. (2008) *Geophys. Res. Lett.*, 35, L05203. [23] Williams, J. T. et al. (2016) *MAPS*, in revision. [24] Franz, H. B. et al. (2014) *Nature* 508, 364-368.